

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**

# PATENT SPECIFICATION

1,013,703



Date of Application and filing Complete  
Specification: September 17, 1963.

1,013,703

No. 36629/63

Application made in Australia (No. 22362) on September 20, 1962.

Complete Specification Published: December 22, 1965.

© Crown Copyright 1965.

Index at Acceptance:—C7 F (1B1B, 2V, 4N); H1 BF.

Int. Cl.:—C 23 c // H01m.

## COMPLETE SPECIFICATION

### NO DRAWINGS

#### Improvements relating to Fuel Cells

We, COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANIZATION, an Australian body corporate established under the Science and Industry Research Act,

5 1949, of 314 Albert Street, East Melbourne, in the State of Victoria, Commonwealth of Australia, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it 10 is to be performed, to be particularly described in and by the following statement:—

This invention relates to improvements in ion exchange membranes for use in membrane-type fuel cells.

15 This type of cell employs an ion exchange resin membrane, either cation or anion type, as a solid electrolyte which also serves to separate two electrode compartments. At one electrode fuel, either gaseous or liquid, 20 is oxidized electrochemically, while at the other electrode oxygen (or air) is reduced electrochemically to promote the oxidation of the fuel. In a hydrogen/oxygen fuel cell with a cation-type membrane the electrode 25 reactions are as follows:

ANODE  $2H_2 \rightarrow 4H^+ + 4$  electrons  
CATHODE  $O_2 + 4H^+ + 4$  electrons  $2H_2O$   
the overall reaction being  
 $2H_2 + O_2 \rightarrow 2H_2O$

30 Other fuels which may be oxidized in a membrane-type fuel cell include hydrazine, methanol, formaldehyde, formic acid as well as carbon monoxide and some hydrocarbon gases such as propane. Oxygen as the oxidant gas may be replaced by air.

The above reactions will not proceed to an appreciable extent unless they are promoted by a catalyst, which is usually one of the noble metals such as platinum, palladium, iridium and rhodium. To be effective such catalyst must be prepared in an extremely finely-divided state (e.g. platinum "black") so that a large surface area is

exposed, with consequent increase in the number of sites at which the reactions can 45 take place. As the cell reactions only take place at the catalyst surface the catalyst itself forms an electrode. Both the cathode and the anode are similarly formed and, in each case, a conductor for electrons, hereinafter 50 called a collector, must be provided which is in intimate contact with the catalyst electrode and which thus serves to conduct electrons through an external circuit.

It is also essential for efficient operation 55 at both electrodes that good contact be maintained between the ion exchange sites in the membrane and the catalyst electrode. In this way transport of hydrogen ions ( $H^+$ ) from the fuel catalyst through the membrane 60 to the oxidant catalyst, where they are required for completion of the reaction, is promoted.

Early fuel cells of the membrane type used platinum (or platinum-plated) gauze 65 on which platinum black was electro-deposited. These were pressed against the ion exchange membrane and acted as catalyst electrodes and also as collectors of electric current. Only small currents, of the 70 order of  $1 \text{ ma/cm}^2$  of the electrode area, were produced from such cells. Later, membranes were developed in which the catalyst was incorporated into the surfaces of the 75 membrane during final resin polymerization.

In the case of a hydrogen/oxygen cell employing a cation exchange resin membrane, the solid membrane electrolyte contains a solution of free acid, as acid-treatment is required to prepare the membrane 80 for use. Also the free acid may assist in promoting migration of  $H^+$ . Each side of the membrane has a thin layer of catalytic "black" incorporated into its surface. Platinum black catalyst is usually chosen as 85 being the most efficient for both electrodes.

[Price 4s. 6d.]

The invention provides a method of producing an ion exchange membrane incorporating a metal catalyst for a membrane-type fuel cell, wherein the metal catalyst is deposited in a finely divided active state in a surface layer of the membrane by chemical reduction in situ of a salt of the metal.

Preferably the metal catalyst is a noble metal but other metals which can be produced by chemical reduction in their salts may also be employed.

In one embodiment of the invention an ionic reducing agent is absorbed on the membrane where it is used to reduce a metal salt in aqueous solution to the metal.

This procedure may be reversed in a further embodiment of the invention, wherein, an ion containing a metal is absorbed on the membrane and subsequently treated with a reducing agent.

The method of the invention also extends to the impregnation of an ion exchange membrane with a metal catalyst comprising two or more of the above mentioned metals, by deposition of the metals in the surface layer of the membrane by the above techniques.

By careful control of variables such as concentration of solutions, temperature and time of treatment, a layer of finely-divided active metal "black" is formed on both surfaces of the membrane. The thickness and depth of penetration of this catalyst layer can be controlled in such a way that efficient electrolytic contact with the membrane ionic sites is achieved, coupled with adequate catalyst loading and low surface resistance.

An advantage of the new process is that commercial membranes of different types, whether heterogeneous or homogeneous, can be quickly impregnated with the catalyst by varying the conditions to suit the type of membrane. This is of particular importance where the membranes are used in small quantities and are individually treated.

A further advantage of the process is the small weight of catalyst required per unit area of surface (degree of loading). Platinum black produced by this method has a high surface area per unit weight and efficient membranes have been prepared containing as little as a mg. of platinum/cm<sup>2</sup> of membrane surface. Low electrical resistance across the surface of the catalyst layer is important in providing efficient electron transfer between catalyst and collector, and the process has

the further advantage of being capable of producing catalyst layers whose surface resistance is less than 1 ohm/1 cm. × 1 cm.

It has been found that the reduction step is best carried out in neutral, alkaline or weakly-acid solution and that, whilst those membranes which have high water uptake absorb a relatively large amount of reductant or metal solution, membranes with low water uptake absorb only a small amount of such solutions. In this latter case it has been found that the amount of such solutions absorbed can be increased by drying the membrane before treatment and also that when only a small amount of reductant is absorbed, a heavier metal deposit is obtained by using a metal solution in which the metal in the ion is in a lower valency state; e.g. PtCl<sub>4</sub><sup>-</sup> (chloroplatinate) in place of the more usual PtCl<sub>6</sub><sup>4-</sup> (chloroplatinate).

The following examples illustrate the method of the invention but it will be understood that no limitation of the scope of the invention is intended or implied thereby.

#### EXAMPLE I

A commercial heterogeneous cation exchange resin membrane having high water uptake (Permutit C20 (Permutit is a trade mark)), in the hydrogen form or in the sodium form, was immersed in a 15 per cent. solution of hydrazine hydrate at 50°C. for 30 minutes. Surplus hydrazine hydrate was removed by rinsing and the membrane was then immersed in a 3% solution of sodium chloroplatinate having a pH value of 3-4. Immersion time was 30 minutes at a temperature of 55-60°C. The membrane was then leached with water to remove free hydrazine and then leached with 1N H<sub>2</sub>SO<sub>4</sub>, to ensure that cation sites were occupied by H<sup>+</sup> ions and to saturate the membrane with free sulphuric acid. The catalyst layers on each side of the membrane were shown by analysis to contain 2-3 mg. of platinum per cm<sup>2</sup>, in a finely divided state having a layer thickness of .01 - .05 mm. and surface resistance of 1.0 ohm/1 cm. × 1 cm.

In a hydrogen-oxygen fuel cell at room temperature with both gases at 2 p.s.i., the above membrane, held between two platinum gauze collectors, had an open circuit voltage of 1.06 v. and current could be drawn as follows:—

10 ma/cm.<sup>2</sup> at 0.74 v. (corrected for iR voltage drop)

110	20	"	0.60	"	"	"	"
	30	"	0.42	"	"	"	"

**EXAMPLE II**

A commercial homogeneous cation exchange resin membrane of lower water uptake than that of Example I (made by Asahi Chemical Industries) in the hydrogen form, was dried at 65-70°C. for 30 minutes and then immersed in a 15% hydrazine hydrate for 16 hours at room temperature (removal of initial water by drying was found to increase absorption of hydrazine). After rinsing to remove surplus hydrazine hydrate the membrane was immersed in either (a) a 3% solution of  $\text{Na}_2\text{PtCl}_6$  adjusted with NaOH to pH 12, or (b) a 2.4% solution of  $\text{Na}_2\text{PtCl}_6$  for 15 minutes at 55-60°C. The membrane was then leached with water followed by leaching with 1N  $\text{H}_2\text{SO}_4$  as in Example I.

The catalyst layers were shown by analysis to contain 2.5 mg. of Pt/cm.<sup>2</sup> and resistance of the surface was 1.2-2 ohms/1 cm.  $\times$  1 cm.

In the fuel cell of Example I at room temperature, open circuit voltage was 1.04 v. and a current of 10 ma/cm.<sup>2</sup> could be drawn at 0.59 v. (corrected for iR voltage drop).

**EXAMPLE III**

A commercial homogeneous cation exchange resin membrane of low water uptake (American Machine & Foundry C. 313), in the hydrogen form, was dried at 65-70°C. for 30 minutes and then immersed in 15% hydrazine hydrate for 16 hours at room temperature. After rinsing to remove surplus hydrazine hydrate the membrane was immersed in 2.4%  $\text{Na}_2\text{PtCl}_6$  at 55-60°C. for 15 minutes. A second treatment consisted of immersion in the above hydrazine hydrate solution at 50°C. for 30 minutes, rinsing to remove surplus hydrazine hydrate and immersion in 2.4%  $\text{Na}_2\text{PtCl}_6$  at 55-60°C. for 15 minutes. The membrane was then leached with water followed by leaching with 1N  $\text{H}_2\text{SO}_4$  as in Example I. The catalyst layers were shown by analysis to contain 1 mg. Pt/cm.<sup>2</sup> and resistance of the surface was 0.5-0.7 ohms/1 cm.  $\times$  1 cm.

In the fuel cell of Example I at room temperature, open circuit voltage was 1.02 v. and a current of 10 ma/cm.<sup>2</sup> could be drawn at 0.58 v. (corrected for iR voltage drop).

Mixed noble metal catalysts were also deposited from chloride solutions by this method, and it was also found that with the very low surface resistance of the catalyst electrodes, the membrane could be made the cathode in an electrolytic cell and further catalyst deposits superimposed electrolytically from pure or mixed metal chloride solutions. Such electrodeposits of mixed noble metals superimposed on chemically deposited catalyst layers were found to be effective electrodes in the hydrogen oxygen fuel cell and, in addition, effective for the

catalytic oxidation of formaldehyde in a formaldehyde-oxygen fuel cell.

**EXAMPLE IV**

A membrane of Example II (Asahi Chemical Industries), after preparation of the catalyst layer by chemical reduction as quoted in the example, was made the cathode in an electrolytic cell containing a solution of platinum and another noble metal, the total metal ion concentration being approximately 1 per cent in 2N hydrochloric acid. At a current density of 12 ma/cm.<sup>2</sup> for 8 minutes at room temperature a mixed metal layer of fine structure was electrodeposited on to the chemically-deposited catalyst layer on each side of the membrane.

In a fuel cell similar to that described, but using a liquid fuel consisting of 1M formaldehyde in 0.5M  $\text{H}_2\text{SO}_4$ , the open circuit voltage was 0.90 v. and a current of 10 ma/cm.<sup>2</sup> could be drawn at 0.37 v. (corrected for iR voltage drop) at a temperature of 25°C.

**WHAT WE CLAIM IS:**

1. A method of producing an ion exchange membrane incorporating a metal catalyst for a membrane-type fuel cell, wherein the metal catalyst is deposited in a finely divided active state in a surface layer of the membrane by chemical reduction in situ of a salt of the metal. 95
2. A method as claimed in Claim 1, wherein the metal catalyst comprises a mixture of two or more metals. 100
3. A method as claimed in Claim 1 or Claim 2, wherein an ionic reducing agent is absorbed into the membrane and the membrane is then treated with an aqueous solution of the metal salt. 105
4. A method as claimed in Claim 1 or Claim 2, wherein an ion containing the metal is absorbed into the membrane and the membrane is then treated with a reducing agent. 110
5. A method as claimed in any of the preceding claims, wherein the reducing agent is hydrazine or a derivative thereof. 115
6. A method as claimed in any one of Claims 1, 3, 4 and 5, wherein the metal catalyst is a noble metal. 120
7. A method as claimed in Claim 6, wherein the metal is platinum. 125
8. A method as claimed in any one of the preceding claims, wherein subsequently to the chemical deposition of the metal catalyst, a further amount of metal is electrolytically deposited in the membrane. 130
9. A method of incorporating a metal catalyst in an ion-exchange membrane substantially as hereinbefore described with reference to any of the Examples I-IV.
10. A catalyst-impregnated ion-exchange membrane when produced by the method claimed in any one of claims 1 to 9.

---

11. A fuel cell incorporating an ion-exchange membrane according to claim 10.

KILBURN & STRODE.

---

Berwick-upon-Tweed: Printed for Her Majesty's Stationery Office by The Tweeddale Press Ltd.—1965  
Published at The Patent Office, 25 Southampton Buildings, London, W.C.2 from which copies may  
be obtained.